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(54) **Promoted tin-antimonate catalysts and use thereof.**

(57) A tin antimonate oxide complex catalyst of the formula:
 $A_aD_bTe_cSn_eSb_fO_x$
 wherein A represents one or more of the following elements: Cu, V, W and or Mo; D represents one or more of the following elements: Bi, Ti, Ge, Ce, La, Cr, Mn, Mg, Ca, Co, Ni, Nb, Ta, Ag, Zn, Cd, K, Cs, U, B, P and Eu; and wherein a is 0.001 to 10; b is 0 to 10; d is 0.001 to 10; e is 0.1 to 10; f is 1 to 20; $f > a + b + d + e$; and x is a number sufficient to satisfy the valence requirements of the other elements present.

These multiply promoted Sn-Sb oxides are superior catalysts for the ammoxidation of olefins to the corresponding unsaturated nitriles, the selective oxidation of olefins to unsaturated aldehydes and acids, and the oxydehydrogenation of olefins to diolefins.

Title

Promoted Tin-antimonate catalysts and use
thereof -----

The present invention relates to novel tin antimonate catalysts and their use in various oxidation-type reactions, such as the oxidation of olefins to produce aldehydes and acids, the
5 amoxidation of olefins to produce unsaturated nitriles and the oxydehydrogenation of olefins to diolefins.

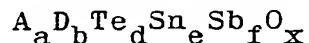
In U.S. 4,035,418, the disclosure of which is incorporated herein by reference, there are
10 described certain promoted tin antimonate catalysts which are useful in various oxidation-type reactions. Although these catalysts give good yields of the desired end products in various oxidation-type reactions, it is always beneficial
15 to provide new catalysts having superior catalytic properties.

Accordingly, it is an object of the present invention to provide new catalysts capable of providing superior yields of desired end products
20 in various types of oxidation reactions.

The present invention which is based on the discovery that certain tin antimonate catalysts when promoted with certain combinations of elements provide excellent yields of desired end products
25 such as, for example, acrylonitrile in various types of oxidation reactions.

Accordingly, the present invention provides

new catalysts for use in various types of oxidation reactions, said catalysts comprising a tin antimonate oxide complex of the formula:



5 wherein A represents one or more of the following elements: Cu, V, W and Mo; D represents one or more of the following elements: Bi, Ti, Ge, Ce, La, Cr, Mn, Mg, Ca, Co, Ni, Nb, Ta, 10 Ag, Zn, Cd, K, Cs, U, B, P and Eu; and wherein a is 0.001 to 10; b is 0 to 10; d is 0.001 to 10; 15 e is 0.1 to 10; f is 1 to 20; f > a + b + d + e; and x is a number sufficient to satisfy the valence requirements of the other 20 elements present.

The present invention also provides an improvement in the known processes for the oxidation of olefins to produce aldehydes and acids, the known processes for the ammoxidation 25 of olefins to produce unsaturated nitriles, and the oxydehydrogenation of olefins to produce diolefins, which comprises using as the oxidation catalyst a tin antimonate catalyst according to the invention.

30 The use of the catalyst in these various different reactions is described below.

Ammoxidation

A wide variety of different reactants can be ammoxidized in accordance with the present 35 invention to produce nitriles. For example, olefins

such as propylene and isobutylene, alcohols such as t-butyl alcohol, and aldehydes such as acrolein and methacrolein can be readily converted to nitriles in accordance with the present invention. In
5 general, compounds which can be converted to nitriles by the ammoxidation reaction according to the invention include 3 to 9 carbon atom hydrocarbons unsubstituted or substituted with oxygen or hydroxyl. Preferred starting materials are
10 olefins, aldehydes and alcohols containing 3 or 4 carbon atoms.

The general ammoxidation process for converting olefins, alcohols and aldehydes to nitriles is well known, and described for example
15 in U.S. Patent 3,546,138, the disclosure of which is incorporated herein by reference. In general, the ammoxidation reaction is accomplished by contacting the reactant, oxygen and ammonia with a particular catalyst in the vapor phase. The
20 reaction according to the invention is carried out in the same manner and under the conditions generally set forth in this patent.

In a preferred aspect, the process according to the invention comprises contacting a mixture
25 comprising propylene or isobutylene, ammonia and oxygen with the promoted catalyst of this invention at an elevated temperature and at atmospheric or near atmospheric pressure.

Any source of oxygen may be employed in this
30 process. For economic reasons, however, it is preferred that air be employed as the source of oxygen. From a purely technical viewpoint, relatively pure molecular oxygen will give similar results. The molar ratio of oxygen to the olefin
35 in the feed to the reaction vessel should be in the

range of 0.5:1 to 4:1 and a ratio of about 1:1 to 3:1 is preferred.

Low molecular weight saturated hydrocarbons do not appear to influence the reaction to an appreciable degree, and these materials can be present; consequently, the addition of saturated hydrocarbons to the reaction feed is within the scope of this invention. Likewise, diluents, such as nitrogen and the oxides of carbon, may be present in the reaction mixture without deleterious effect.

The molar ratio of ammonia to olefin in the feed to the reactor may vary between about 0.05:1 to 5:1. There is no real upper limit for the ammonia/olefin ratio, but there is generally no reason to exceed the 5:1 ratio. At ammonia/olefin ratios appreciably less than the stoichiometric ratio of 1:1, various amounts of oxygenated derivatives of the olefin will be formed.

Significant amounts of unsaturated aldehydes, as well as nitriles, will be obtained at ammonia-olefin ratios substantially below 1:1, i.e., in the range of 0.15:1 to 0.75:1. Above the upper limit of this range, the amount of aldehydes produced rapidly decreases. It is fortuitous that within the ammonia-olefin range stated, maximum utilization of ammonia is obtained and this is highly desirable. It is generally possible to recycle any unreacted olefin and unconverted ammonia.

Water can also be included in the feed although it is not essential. In some instances, e.g. fixed-bed systems, water may improve the selectivity of the reaction and the yield of nitrile. However, reactions not including water

in the feed are also within the scope of the present invention.

In general, the molar ratio of added water to olefin, when water is added, is in the neighborhood of 0.1:1 or higher. Ratios on the order of 1:1 to 6:1 are particularly desirable, but higher ratios may be employed, i.e. up to about 10:1.

The reaction is carried out at an elevated temperature such as 200°C to 600°C, preferably 400°C to 500°C. The pressure at which the reaction is conducted is also an important variable, and the reaction should be carried out at about atmospheric or slightly above atmospheric (2 to 3 atmospheres (2 to 3 kg/cm²)) pressure. In general, high pressures, i.e. above 15 atmospheres, (15 kg/cm²), are not suitable since higher pressures tend to favour the formation of undesirable byproducts.

The apparent contact time is not critical, and contact times in the range of from 0.1-50 seconds may be employed. The optimal contact time will, of course, vary depending upon the reactant being used, but in general, contact time of from 1-15 seconds is preferred.

The ammoxidation reaction according to the invention is carried out in the vapor phase. Normally, the process is conducted on a continuous basis using either a fixed-bed or a fluid-bed catalyst. However, a batch operation can be employed.

The reaction product passing out of the reactor is normally in the form of a gas. Conventionally, this gaseous reaction product is treated to remove NH₃ and then partially condensed

either by indirect contact with a cooling medium or direct contact with water to form a liquid phase containing acrylonitrile, acrolein, acrylic acid, HCN and acetonitrile and a vapor phase
5 containing CO₂, CO, N₂ and O₂. The acrylonitrile is then separated from the liquid phase by a number of different techniques such as, for example, distillation or water extraction/distillation. Additional steps can be employed to separately
10 recover HCN and/or acetonitrile from the gross reaction product.

Oxidation

As previously indicated, the catalysts of this invention can also be employed in the
15 catalytic oxidation of olefins to various different reaction products.

The reactants used in the oxidation to oxygenated compounds are oxygen and an olefin such as propylene, isobutylene and other olefins
20 having up to three contiguous carbon atoms (i.e. three carbon atoms arranged in a straight chain).

The olefins may be in admixture with paraffinic hydrocarbons, such as ethane, propane, butane and pentane; for example, a propylene-propane mixture
25 may constitute the feed. This makes it possible to use ordinary refinery streams without special preparation.

The temperature at which this oxidation is conducted may vary considerably depending upon
30 the catalyst, the particular olefin being oxidized and the correlated conditions of the rate of throughput or contact time and the ratio of olefin to oxygen. In general, when operating at pressures near atmospheric, i.e. 0.1 to 10 atmospheres (0.1 to
35 10 kg/cm²), temperatures in the range of 150°C to

600°C may be advantageously employed. However, the process may be conducted at other pressures, and in the case where superatmospheric pressures, e.g. above 10 atmospheres (10 kg/cm²) are employed,

5 somewhat lower temperatures are possible. In the case where this process is employed to convert propylene to acrolein, a temperature range of 200°C to 500°C has been found to be optimum at atmospheric pressure.

10 While pressures other than atmospheric may be employed, it is generally preferred to operate at or near atmospheric pressure, since the reaction proceeds well at such pressures and the use of expensive high pressure equipment is avoided, and
15 formation of undesired byproducts and waste is diminished.

The apparent contact time employed in the process is not critical and it may be selected from a broad operable range which may vary from
20 0.1 to 50 seconds. The apparent contact time may be defined as the length of time in seconds which a unit volume of gas measured under the conditions of reaction is in contact with the apparent unit volume of the catalyst. It may be
25 calculated, for example, from the apparent volume of the catalyst bed, the average temperature and pressure of the reactor, and the flow rates of the several components of the reaction mixture.

The optimum contact time will, of course, vary
30 depending upon the olefin being treated, but in the case of propylene and isobutylene, the preferred contact time is 0.15 to 15 seconds.

A molar ratio of oxygen to olefin between about 0.5:1 to 5:1 generally gives the most satisfactory
35 results. For the conversion of propylene to

acrolein, a preferred ratio of oxygen to olefin is from about 1:1 to about 2.5:1. The oxygen used in the process may be derived from any source; however, air is the least expensive source of oxygen and is preferred for that reason.

The addition of water to the reaction mixture in oxidation reactions can have a beneficial influence on the conversion and yields of the desired product especially in fixed-bed reactions.

The manner in which water affects the reaction is not fully understood. In any event, it is preferred in fixed-bed operation to include water in the reaction mixture, and in general a ratio of olefin to water in the reaction mixture of from 1:0.25 to 1:10 will give very satisfactory results while a ratio of 1:0.5 to 1:6 has been found the optimum when converting propylene to acrolein.

Inert diluents such as oxygen and carbon dioxide, may be present in the reaction mixture.

Oxydehydrogenation

In accordance with the present invention, the promoted catalyst system of the present invention can also be employed in the catalytic oxidative dehydrogenation of olefins to diolefins and aromatic compounds. In this process, the feed stream in vapor form containing the olefin to be dehydrogenated and oxygen is conducted over the promoted catalyst at a comparatively low temperature to obtain the corresponding diolefin.

By the term "olefin" as used herein is meant open chain as well as cyclic olefins. The olefins dehydrogenated in accordance with this invention have at least four and up to about nine nonquaternary carbon atoms, of which at least four are arranged in series in a straight chain or ring. The olefins

preferably are either normal straight chain or tertiary olefins. Both cis and trans isomers, where they exist, can be dehydrogenated.

Among the many olefinic compounds which can be dehydrogenated in this way are butene-1; butene-2; pentene-1; pentene-2; pentenes, hexenes, etc. such as 2-methylpentene-1, 3-methylbutene-1, 3,4-dimethyl-pentene-1, 4-methyl-pentene-2; heptene-1; octene-1; cyclopentene; cyclohexene, 3-methyl cyclohexene and cycloheptene.

Open chain olefins yield diolefins, and, in general, six-membered ring olefins yield aromatic ring compounds. The higher molecular weight open chain olefins may cyclize to aromatic ring compounds.

The feed stock in addition to the olefin and oxygen can contain one or more paraffins or naphthenic hydrocarbons having up to about ten carbon atoms, which may be present as impurities in some petroleum hydrocarbon stocks and which may also be dehydrogenated in some cases.

The amount of oxygen can be within the range of from about 0.3 to about 4 moles per mole of double-bond created. Stoichiometrically, 0.5 mole of oxygen is required for the dehydrogenation of one mole of monolefin to a diolefin. It is preferred to employ an excess of oxygen, e.g. an oxygen/olefin ratio of from 0.6 to about 3, in order to ensure a higher yield of diolefin per pass. The oxygen can be supplied as pure or substantially pure oxygen or as air.

When pure oxygen is used, it may be desirable to incorporate a diluent in the mixture such as steam, carbon dioxide or nitrogen.

The feed stock can be catalytically dehydrogenated

in the presence of steam, but this is not essential. When steam is used, from about 0.1 to about 6 moles of steam per mole of olefin reactant is employed, but amounts larger than this can be used.

5 The dehydrogenation proceeds at temperatures within the range of from about 200°C to about 1,000°C. Optimum yields are obtainable at temperatures within the range from about 300°C to 600°C.

10 The preferred reaction pressure is approximately atmospheric, within the range of from about 0.1 to about 5 atmospheres.

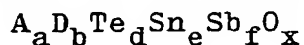
Only a brief contact time with the catalyst is required for effective dehydrogenation. The
15 apparent contact time with the catalyst can vary from about 0.1 up to about 50 seconds but higher contact times can be used if desired. At these contact times, comparatively small reactors and small amounts of catalyst can be used effectively.

20 Process Conditions

In carrying out the foregoing process, any apparatus of the type suitable for carrying out oxidation reactions in the vapor phase may be employed. The processes may be conducted either
25 continuously or intermittently. The catalyst may be a fixed-bed employing a large particulate or pelleted catalyst or, in the alternative, a fluid-bed catalyst may be employed.

Catalyst

30 The catalysts employed in accordance with the present invention are oxide complexes of tin and antimony promoted with various additional elements and can be described by the general formula:



35 as defined herein.

-11-

The catalysts of this invention are substantially iron free, preferably iron free. Also, it is preferred that these catalysts contain at least two of the A elements, and that D is one
5 or more of the following elements:- Bi, Ti, Ge, Ce, La, Cr, Mn, Mg, Co, Ni, Nb, Zn, K and Cs.

For all of the above catalysts, it is preferred that a is 0.05 to 5, preferably 0.1 to 2.5 based on 12 atoms of antimony, i.e. f is 12.
10 In addition, it is preferred that the Te/Sb ratio be within 0.1 to 2, preferably 0.3 to 1 based on 12 atoms of antimony. Moreover in all catalysts it is preferred that the Sn/Sb ratio is 1/5 to 1/1.1, more preferably 1/5 to 1/2.

15 These catalysts can be used either in unsupported form or supported on suitable carriers such as SiO_2 , Al_2O_3 , BPO_4 , SbPO_4 , ZrO_2 , Alundum and the like. The catalysts can also be coated on these supports by special techniques known in the
20 art.

These catalysts can be prepared by conventional techniques such as disclosed in the previously
25 mentioned U.S. 4,035,418.

The following Examples illustrate the invention
25

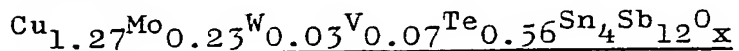
EXAMPLES

In these Examples where the ammoxidation of propylene to acrylonitrile is described the term
30 "% yield" means

$$\frac{\text{moles product formed}}{\text{moles reactant fed}} \times 100$$

In each of the examples and working example, a catalyst having a composition set forth in the

following table was prepared in accordance with a standard laboratory preparation. For example, the catalyst of Example 3 was prepared as follows:



- 5 74.96 gms. Sb_2O_3 was oxidized by the addition of about 3 times its weight of HNO_3 with stirring and heating in a reflux apparatus for approximately 5 hours. 400 ml. of water was added and 20.35 gms. of granular tin was added slowly and heated and
- 10 stirred for approximately $2\frac{1}{2}$ hours until no tin metal was visible in the slurry. The slurry was filtered, and water added to the solids to form a new slurry. 13.12 gms. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.39 gms. 85% WO_3 and 1.76 gms. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were
- 15 dissolved in water and added to the slurry. 0.26 gms. V_2O_5 was dissolved in water and a small amount of oxallic acid. 3.88 gms. TeO_2 was partially dissolved in HNO_3 . The vanadium and tellurium were then added to the slurry carefully due to the
- 20 danger of a violent reaction between them. The pH of the system was adjusted to 6 ± 2 using ammonium hydroxide and the slurry was then evaporated to a paste and then put in a drying oven at 130°C for about 20 hours with frequent
- 25 mixing for the first 4 hours. The dried powder obtained was then dentrified by heating it 3 hours at 290°C in air and further heating it for 3 hours at 425°C . The catalyst was then calcined in air at 820°C for 3 hours. The calcined catalyst
- 30 was then ground and crushed and the portion having a particle size between 20 and 35 mesh recovered as the catalyst.

- 35 The catalyst of Example 9 was prepared in the same way except that Cu, Te and Sn metals were dissolved in nitric acid, oxidation of Sb_2O_3 in

nitric acid as a separate step being eliminated. —

In each of the examples and in the comparative example A, B and C, 5 cc. of the catalyst was charged into a 6 cc. reactor and contacted with a feed comprising $1\text{C}_3\text{H}_8/1.2\text{NH}_3/10.5\text{air}/4\text{H}_2\text{O}$ at elevated temperature.

The composition of the catalysts, the final calcination temperature, the reaction temperature and the results obtained are set forth in the following table.

TABLE

<u>Example</u>	<u>Catalyst Composition</u>	<u>Cal Temp</u>	<u>React Temp</u>
Comp A	$\text{Sn}_1\text{Sb}_3\text{O}_x$	800	430
15 Comp B	$\text{Sn}_1\text{Sb}_3\text{O}_x$	820	460
Comp C	$\text{Cu}_{1.27}\text{Mo}_{0.23}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460
1	$\text{Mo}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	820	460
2	$\text{Cu}_{1.27}\text{Mo}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460
3	$\text{Cu}_{1.27}\text{Mo}_{0.23}\text{W}_{0.03}\text{V}_{0.07}\text{Te}_{0.57}\text{Sn}_4\text{O}_x$	820	460
20 4	$\text{Cu}_{1.27}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	820	460
5	$\text{Mo}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460
6	$\text{Cu}_{1.83}\text{Mo}_{0.23}\text{Te}_{0.33}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460
7	$\text{Cu}_{1.27}\text{W}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460
25 8	$\text{Cu}_{1.27}\text{Mo}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x + 20\% \text{TiO}_2$	800	460
9	$\text{Cu}_{1.27}\text{W}_{0.23}\text{Te}_{0.57}\text{Sn}_4\text{Sb}_{12}\text{O}_x$	800	460

TABLE (Contd.)

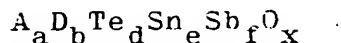
Example	Yields	
	AN	HCN
Comp A	51.1	6.2
5 Comp B	61.5	7.3
Comp C	59.1	4.5
1	65.3	6.6
2	73.7	5.2
3	74.9	4.6
10 4	67.6	2.8
5	67.7	6.1
6	73.2	5.6
7	76.8	4.6
8	65.8	1.5
15 9	78.0	4.5

From the foregoing, it can be seen that the catalyst according to the invention provides significant and superior yields of acrylonitrile when used in the conventional ammoxidation reaction. Thus, these catalysts are of significant commercial interest in this field. Moreover, these catalysts are also advantageous because they provide easy adjustment of the acrylonitrile/HCN yields ratio via minor compositional changes, they are redox stable and they provide an environmentally acceptable effluent (i.e. a byproduct effluent with a very low COD).

Although only a few embodiments of the present invention have been described above, it should be appreciated that many modifications can be made without departing from the spirit and scope of the invention. All such modifications are intended to be included within the scope of the present invention, which is to be limited only by the following claims.

CLAIMS:

1. A tin antimonate oxide complex catalyst of the formula:



wherein A represents one or more of the following elements: Cu, V, W and or Mo;

D represents one or more of the following elements: Bi, Ti, Ge, Ce, La, Cr, Mn, Mg, Ca, Co, Ni, Nb, Ta, Ag, Zn, Cd, K, Cs, U, B, P and Eu; and

wherein a is 0.001 to 10;

b is 0 to 10;

d is 0.001 to 10;

e is 0.1 to 10;

f is 1 to 20;

$f > a + b + d + e$; and

x is a number sufficient to satisfy the valence requirements of the other elements present.

2. A catalyst as claimed in claim 1 characterised in that it contains at least two of the A elements.

3. A catalyst as claimed in claim 2 characterised in that b is at least 0.001.

4. A catalyst as claimed in any of claims 1 to 3 characterised in that D represents one or more of the following elements Bi, Ti, Ge, Ce, La, Cr, Mn, Mg, Co, Ni, Nb, Zn, K and Cs.

5. A oxide complex catalyst as claimed in any of claims 1 to 4 characterised in that f is 12, and a is 0.5 to 5.

6. A catalyst as claimed in claim 5 characterised in that Te/Sb is 0.1-2.

7. A catalyst as claimed in any of claims 1 to 6 characterised in that Sn/Sb is 1/5 to 1/1.1

8. An ammoxidation process for producing a nitrile wherein a reactant which is an olefin, an aldehyde and/or an alcohol and oxygen and ammonia are contacted in the vapor phase with a catalyst at elevated temperature, characterised in that the catalyst used is a catalyst as claimed in any of claims 1 to 7.

9. A process as claimed in claim 8 characterised in that the reactant is propylene and/or isobutylene.

10. An oxidation process for oxidizing an olefin comprising contacting an olefin having no more than 13 contiguous carbon atoms and oxygen in the vapor phase at elevated temperature with a catalyst characterised in that the catalyst used is a catalyst as claimed in any of claims 1 to 7.

11. An oxydehydrogenation process comprising contacting an olefin having 4 or more contiguous carbon atoms and oxygen at elevated temperature in the vapor phase with a catalyst, characterised in that the catalyst is a catalyst as claimed in any of claims 1 to 7.



European Patent
Office

EUROPEAN SEARCH REPORT

0031693
Application number
EP 80 30 4631

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 1 518 636 (PRODUITS CHIMIQUES UGINE KUHLMANN) * Claims 1-8; example *	1,2,5-9	B 01 J 27/02
	--		
X	EP - A - 0 000 564 (STANDARD OIL) * Claims 1-4,6 *	1-10	
	--		
D	US - A - 4 035 418 (OKADA et al.) * Claims 1-3; abstract *	1-7, 10, 11	TECHNICAL FIELDS SEARCHED (Int. Cl.)
	--		
X	US - A - 4 083 804 (SAITO et al.) * Abstract; claims 1-4; column 13, table 1; catalyst 16 *	1-9	B 01 J 27/02
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	US - A - 4 049 575 (SASAKI et al.) * Column 1, lines 7-12; claims 1-22; column 15, lines 6-23 *	1-11	
	--		
X	US - A - 3 893 945 (KOBAYASHI et al.) * Claims 1-5; abstract *	1-7, 10	CATEGORY OF CITED DOCUMENTS
	--		
X	US - A - 4 151 117 (SCHLAEFER) * Abstract; claims 1-9 *	1-7, 10	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons

The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 30-03-1981	Examiner MICHIELS

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